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Note

IR and X-ray studies on nickel ferrite with rare earth doping

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Abstract : The nickel ferrite of composition $Ni_{(x)}Fe_{(3-x)}O_4$ with x = 0.3, 0.5, 0.7, 0.9 doped with neodymium and gadolinium were studied by infrared absorption spectroscopy. The IR spectrum showed two main absorption bands ν_1 and ν_2 in the range of 400cm^{-1}-600cm^{-1} arising from the octahedral and tetrahedral complexes. The positions of absorption bands are compositional dependent whose dependence could be attributed to the variation in cation – oxygen bond distances. The force constant of tetrahedral and octahedral sites supports cation distribution. With the addition of gadolinium absorption bands ν_1 and ν_2 were found to be broadened and the peaks are diffused. The lattice constants were found to decrease with the addition neodymium and gadolinium.

Keywords Ferrites, infrared spectra, interionic distances

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The infrared spectroscopy is an important and nondestructive characterising tool which provides qualitative information regarding structural details of crystalline material [1]. This technique is based upon the fact that a chemical substance shows marked selective absorption in the infrared region. The results from IR absorption study can be used to interpret the electrical and magnetic properties of the ferrites [2]. The various absorption bands present in the spectrum represent the details regarding functional groups and their linkages can be explored. They are found to be dependent on atomic mass, cationic radius, cation – anion bond distances, cation distribution *etc*. Infrared spectral analysis have been carried out for several ferrites and reported two absorption bands within the wavenumbers (800 – 200)cm^{-1} [3], which are attributed to the tetrahedral and octahedral group complexes of the spinel structure, respectively. The IR spectra of some mixed Co-Zn and Mg-Zn ferrites have also been reported [4]. Far IR spectral studies of mixed Li-Zn ferrites were also made by Ravinder [5]. He had correlated ν_1, ν_2 and ν_3 bands to the Fe^{2+} ion concentration. IR absorption spectroscopy and the results showing the compositional dependence of force constant, are attributed to the cation oxygen bond distances. The structural distortion in case of chromium substituted nickel ferrite has been studied [7]. The IR spectra of Cd, Co, Mg, Ni, Zn, Cu *etc* containing ferrites have been reported [8,9]. The X-ray studies for zinc substituted Ni-Pb ferrites was studied by Sable *et al* [10]. In this work, we have reported analysis for IR spectra and X -ray studies of $Ni_x Fe_{3-x} O_4$ spinel ferrite system in nanophase with x = 0.3, 0.5, 0.7 and 0.9 and doped with neodymium & gadolinium.

The samples having general chemical formula $Ni_x Fe_{3-x} O_4$ (where x = 0.3, 0.5, 0.7 and 0.9) were prepared by taking the necessary amount of nickel chloride and iron powder according to the stoichiometric ratio $Ni_x Fe_{3-x} O_4$.

The weighed chemicals were dissolved in dilute H_2SO_4 and heated slowly to evaporate the solvent. The remaining mire was transferred into a porcelain crucible and was kept in a furnace and heated in air for four hrs at 500^{0}C. Then it was allowed to cool slowly, till the room temperature is reached. The fired sample was grinded to fine powder and was again heated to 950^{0}C for two hrs. After cooling, it was grinded to a fine powder.

To confirm the completion of molecular state reaction, the samples were subjected to characterization by X-ray diffraction and Infra-red absorption spectroscopy. The IR absorption spectra of finely crushed powder of the sample were obtained in

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the range of 1000 cm^{-1} to 200 cm^{-1} by using FITR – SHIMADZU Spectrophotometer model 8700 where KBr is used as the medium. The spectrum, transmittance (%) against wave number (cm^{-1}), is used for interpretation of the results. X-ray diffractograms were taken using Rigaku-mini flex system with Cu-kα radiation of wavelength 1.5418 Å. Ni- filter was used. The sample was scanned between $80^0$and 2^0.

The powdered sample $Ni_xFe_{3-x}O_4$ under investigation reveals the formation of single phase cubic spinel structure showing well defined reflection from allowed planes. From the X-ray diffraction peaks, average particle size was estimated using Scherrer's formula ($t = 0.9\lambda / B\cos\theta$. where t = particle size of the crystal, λ = wavelength of the Cu-kα radiation, B = full width at half maximum of the diffraction peak taken in radians), it was found to be in the range of 19 to 32 nanometers for all the samples. Lattice constants of the samples with and without impurities are given in Table 1 below. The variation of concentration and lattice constant was found to be a straight line for nickel ferrites. Usually in a solid solutions of spinels within the miscibility range, a linear change in lattice constant with concentration of the component is observed [11]. With the addition of impurities, their lattice constants were found to decrease. Due to Nd^{3+} -substitution, the lattice constant is found to decrease slightly. Such reduction in the lattice constant in rare –earth substituted ferrites system was also reported [12,13].

Table 1. Lattice constant (a) for pure nickel and doped nickel ferrite

Conc $Ni^{2+}(x)$	a (A^0)	Conc Ni^{2+}(doped)	a(A^o)
0.3	3 6944	0 3(Nd)	3.7777
0 5	3.8801	0.5(Nd)	3.7148
0.7	3.9195	0.7(Gd)	3 8554
0.9	3.8019	0 9(Gd)	3.7607

FTIR absorption spectra for all samples are obtained from IR spectrophotometer and the typical spectra for the sample x = 0.5 is given in Figure 1.

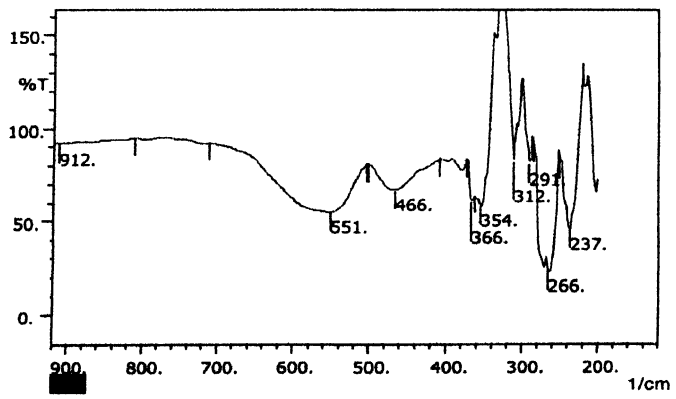

Figure 1. Infra red absorption spectra for compositions $Ni_{(0.5)}$ $Fe_{(3-0.5)}O_4$.

It is found that spectra consist of two significant absorptio bands, one around 550cm^{-1} and the other around 460cm Absorption bands observed (Tables 2, 3) in this range ar characteristics of spinel structure having two sublattice tetrahedral (A) site and octahedral (B) site [3].

Table 2 Position of IR absorption bands (ν_1, ν_2) for nickel ferrite

Conc $Ni^{2+}(x)$	ν_1 (cm^{-1})	ν_2 (cm^{-1})
0.3	547.7	468 7
0.5	551.6	466 7
0 7	555 5	472 5
0 9	569 0	474 5

Table 3. Position of IR absorption bands (ν_1, ν_2) for doped nickel ferri

Conc $Ni^{2+}(x)$	ν_1(cm^{-1})	ν_2(cm^{-1})
0.3	549.7	472 5
0 5	553.5	404 1
0.7	551.6	444 6
0 9	569.9	364 5

The absorption band ν_1, observed at around 550cm $^{-1}$, is du to metal oxygen stretching vibrational modes and it is attributa to Fe^{3+}– O^{2-} vibrations at the tetrahedral site, whereas observed at 460cm^{-1} is assigned to octahedral Fe^{2+}– O^{2-} grou complexes [4]. It was found that the positions of bands ar composition -dependent. These two bands are sharp and stron in intensities.

It was observed that for nickel ferrites without impurities the absorption bands ν_1 and ν_2 were increasing with the increa in concentration of Ni but for doped ferrites, the absorptio bands were found to decrease. The absorption bands observe in 310 , 268cm^{-1} are identified to be the peaks of ν_4 and ν_3 for th samples without impurity[14]. For the doped samples, mor number of peaks are observed due to the splitting of ν_4 and bands by the doping ions. The peaks observed around 55 cm^{-1} and 460cm^{-1} are not sharp for the doped samples Th broadening of the bands is due to addition of gadolinium in th samples of Ni ferrites of concentration (x= 0.7 and 0.9) .This fac is also supported by Srivastav and Srinivasan [8].

On substitution of Nd^{3+} and Gd^{3+} ,the position of ν_2 band shift towards lower side, which suggests the occupancy of Nd and Gd^{3+} Octahedral (B) site. However on substitution o impurities as said before broadening of ν_2 band take place whic may be due to occupancy of cations of different character o the same site,

by the relation $\nu = 1/2\pi \quad (K/M)^{1/2}$,

ν = Vibrational frequency of the ion,

K = force constant of the ion,

M = reduced mass of the ion.

The decrease in vibrational frequencies indicates that the ond length decreases. It is found to decrease the octahedral rce constant which supports the occupancy of neodymium nd gadolinium on B site. The compositional dependence of rce constants are attributed to the cation oxygen bond istances [6].

The results obtained from IR absorption spectra of the amples under investigation, reveal cubic spinel structure howing two significant absorption bands.

(i) The absorption bands ν_1 and ν_2 are found in the expected range and the difference in band positions is due to the difference in the Fe^{3+} - O^{2-} for the octahedral and tetrahedral complexes.

(ii) The positions of the absorption bands are composition-dependent which could be attributed to the variation in cation – oxygen bond distances.

(iii) Variations in the force constant of tetrahedral and octahedral sites support predicted cation distribution, where in adding gadolinium, and the absorption bands ν_1 and ν_2 were found to be broadened and the peaks are diffused.

The lattice constants were found to decrease by the addition neodymium and gadolinium.

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